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N. Yang and Y. Deng

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# **SIZE MECHANISM OF POLYSTYRENE-BASED CATIONIC COPOLYMERS (PSCC)**

Ning Yang and Yulin Deng

Institute of Paper Science and Technology, 500 10th Street N.W., Atlanta, GA 30318, U.S.A.

## **ABSTRACT**

A series of polystyrene-based cationic copolymers (PSCC) were synthesized by copolymerization of styrene and cationic comonomer vinylbenzyl trimethylammonium chloride (VBTMAC). These copolymers can be used as internal paper-sizing agents. The results showed that the hydrophobicity of handsheets could be significantly improved by PSCC and the sizing performance was a function of addition rate, curing time, and pH conditions. The sizing efficiency was directly correlated with the actual amount of PSCC in the handsheet. Significant paper sizing was obtainable only when the full coverage of polymer was reached.

Heat treatment was essential for PSCC sizing. The role of heating was to increase the spreading of size particles over the fiber surface. The evidence from SEM observation supported this hypothesis.

## **INTRODUCTION**

Cellulosic materials usually are hydrophilic; therefore, paper fibers have a strong natural tendency to interact with water. Paper products like towels and tissues absorb water rapidly. However, for many paper grades designed for use in writing, printing,

packaging, and construction, liquid repellency is essential. Sizing is the process of making papers more water resistant by using sizing agents during papermaking. The commonly used sizing agents include rosin-based natural sizes and synthetic sizes such as alkylketene dimer (AKD) and alkenyl succinic anhydride (ASA). The North American market for these sizing agents exceeded 250 million pounds in 1999 [1]. The worldwide demand is estimated around \$300 million in sales of rosin sizes and \$250 million in sales of synthetic sizes, with annual market growth of between 4% and 5%.

However, the commercially used sizing agents cannot fully satisfy the papermaker's requirements. It is well known that rosin-based sizing agents are restricted to use only under acidic conditions. Although AKD and ASA can be used for alkaline papermaking, some problems, such as paper slipperiness, low emulsion instability, hydrolysis, deposition on the paper machine, and sizing reversion, often occur during papermaking.

To be a potential sizing agent, the material must meet certain criteria. It must be highly hydrophobic, have high retention on the fibers, distribute uniformly, and be chemically stable with penetrants [2, 3]. The polymeric sizing agent is a new member in the family of sizing materials. Polymer sizes have some advantages over conventional sizes, such as high hydrophobicity, good stability, and ease of modification. Much research has been undertaken in this area [4-8].

For the present study, a polystyrene-based cationic copolymer (PSCC) was chosen as the internal sizing agent. Pure polystyrene is a hydrophobic material. In order to get a uniform distribution onto fiber surfaces, small particles of the polymer must be prepared.

In addition, these particles should be able to attach to fibers. Recent studies reported that cationically charged polystyrene latexes are effective papermaking retention aids and sizing agents [9-12]. The cationic nature enables the adhesion between polymer and fibers. In order to improve the uniformity of the polymer adsorption and diffusion on wood fiber surfaces, the particle size of PSCC should be less than 100 nm [10]. Both emulsion and microemulsion polymerization techniques have been used for cationic latex preparation in previous works [9-12]. However, it was found that the conventional emulsion polymerization technique is difficult to use for preparing such small particles. Although the microemulsion technique has been successfully used, the high surfactant concentration used in microemulsion polymerization will reduce the hydrophobicity of wood fibers, which gives a negative effect on the paper sizing. Furthermore, the high dosage of surfactant will increase the cost. In this work, a new approach for preparing very small particles of PSCC was reported.

To consider a material a good sizing agent, it should meet the criteria mentioned earlier. A polystyrene-based cationic copolymer (PSCC) could meet these requirements well. First, cationic repeat units along the polymer molecule would serve as a retention aid. Second, polystyrene would provide high hydrophobicity. Finally, uniform distribution could be achieved through small particles of sizes that can be controlled by polymerization techniques. Based on the above assumptions, a series of PSCC copolymers were synthesized. Their colloid properties had been reported in a previous publication [13]. In the present study, the PSCC sizing performance on handsheets was evaluated as a function of polymer addition rate, curing time, and the pH condition in which the

handsheets were prepared. To understand the polymer sizing mechanism from a fundamental point of view, efforts were made to measure the absolute polymer retention value on handsheets. In further study, water contact angles on PSSC coated glass were detected in order to investigate polymer coverage on an anionic hydrophilic surface. Finally, the rheological behavior was observed by SEM technology.

## **EXPERIMENTAL**

### **Material**

Styrene (Aldrich) was used as the monomer for copolymerization. The cationic comonomer vinylbenzyl trimethylammonium chloride (VBTMAC, m/p 60/40, Acros Organics) and cationic water-soluble initiator 2, 2'-azobis (2-methylpropionamidine) dihydrochloride were applied as received. Analytical-grade Ethanol was used as solvent. Bleached kraft softwood (BKS) pulp was used for handsheet making.

### **Polymer Synthesis**

Copolymers of styrene and VBTMAC were synthesized by direct copolymerization of the two materials in ethanol. The details for the copolymer preparation were published previously [13]. In a typical polymerization process, a three-necked glass reactor equipped with a magnetic stir was filled with 150 mL ethanol and an appropriate amount of styrene and VBTMAC. The solution was flushed with nitrogen for 30 minutes and thermostated at 60°C. After stabilization of temperature, the initiator was dissolved in 5 mL deionized water and injected into the reactor. The reaction was carried out under nitrogen for 6 hours with constant stirring. Finally, the solvent and excess monomers were removed by

distillation under reduced pressure at 35°C. The synthesis conditions are summarized in Table 1.

### **Colloid Dispersion Preparation**

A polystyrene-based cationic copolymer (PSCC) was dispersed in boiled water until a stable colloid dispersion was reached.

### **Handsheet Preparation and Sizing Test**

Bleached softwood kraft (BSK) pulp was used in this study. The pulp was well dispersed and diluted to a consistency of 0.3%. The pH value was adjusted before adding PSCC. The stock was then stirred for 30 s and allowed to stand for another 2 min. The handsheet was made according to TAPPI Method T 205 and dried in dryer at 105°C. The heating time varied from 2 to 30 min based on the experimental design. The handsheet sizing was evaluated by the Hercules Sizing Test (HST). It was conducted at 80% reflectance by using a 1% formic acid ink solution.

### **UV/VIS Diffuse Reflectance Spectroscopy**

UV/VIS spectra were recorded on a Perkin Elmer Lambda 190 DM spectrophotometer equipped with a diffuse reflectance and transmittance accessory (Labsphere RSA-PE-90). The accessory is essentially an optical bench that includes double beam-transfer optics and a six-inch-diameter (154 mm) integrating sphere. Background correction was made with control handsheets which retained no PSCC.

### **Water Contact Angle Measurement**

In order to coat PSSC within a defined area on a glass surface, first, the selected glass slide was thoroughly cleaned; then, a self-adhesive vinyl tile was cut into 4cm x 4cm squares. A one-inch hole was punched out on each square. Then the punched square was adhered on the cleaned glass slide, leaving an open area with 1-inch diameter. The desired amount of PSSC dispersion was dispersed within this area. After air drying, water was completely evaporated and only PSSC was deposited within the defined area on glass surface. The coated glass slide was then heated overnight at 105°C. The FTA-200 Dynamic Contact Angle Analyzer was used to measure the water contact angle of the polymer-coated sample.

### **SEM Observation**

The JEOL JSM-6400 scanning electron microscope (SEM) was applied to study PSSC rheological behavior with the effect of heating. Before the sample preparation, the Fisher Scientific 18-mm round glass cover was thoroughly washed by detergent and distilled water. Then, the cleaned glass was coated with a drop of PSSC colloidal dispersion and dried in the air. Because of the nonconductive nature, the PSSC coated glass was handled with special care: (1) the coated glass was stuck onto the metal sample stub with double-sided conductive carbon tape; (2) then, the sample was coated with Au/Pt by using Hummer V Sputter Coater; (3) finally, the carbon adhesive was spread around the edge of the glass in order to increase the conductivity of the flat sample. The SEM sample preparation is illustrated in **Figure 1**. The observation was made before and after the sample being heated at 105 and 195°C.



## RESULTS/DISCUSSION

### Possible Mechanism

PSCC is a random copolymer of styrene and cationic comonomer vinylbenzyl trimethyl ammonium chloride. The polymerization reaction and chemical structure is illustrated in **Figure 2**. The possible mechanism of copolymer aggregate formation and paper sizing development with the cationic polystyrene-based copolymer is schematically shown in **Figure 3**. Because the copolymers contain a water-insoluble styrene backbone and different contents of cationically charged monomers, the copolymers can be either water soluble or insoluble depending on the charge density, molecular weight, and structure. PSCC is a typical cationically charged hydrophobic copolymer. The hydrophobic polystyrene tends to aggregate, and the hydrophilic VBTMAC tends to dissolve in water. As a result, this copolymer is expected to form stable colloids in water if the hydrophobic/hydrophilic forces are well balanced. Because these particles are cationically charged, they can be adsorbed onto negatively charged wood fibers. When the temperature increases to the glass transition temperature or melting temperature, the copolymer diffuses along the fiber surface and finally forms a hydrophobic layer on fiber surfaces by which the paper is sized.

### Paper Sizing with PSCC

Based upon the above discussion, it is suggested that PSCC could be used as an internal sizing agent. **Figure 4** shows the typical results of PSCC sized handsheets. In

these experiments, the addition rate of PSCC ranged from 0.1% to 0.5% based on dry fiber weight, and the sized handsheets were cured at 105<sup>0</sup>C for 30 minutes. It can be seen that the sizing efficiency was increased significantly when the addition rate of polymer increased from 0.3% to 0.5%. With 0.5% polymer addition, the HST value was more than 3000 s, showing that PSCC could be an effective sizing agent.

It is thought that, when the PSCC dispersion is added to pulp, the cationically charged polymer microaggregates adsorb onto fiber surfaces. As the polymer is heated to above the glass transition temperature ( $T_g$ ), it melts and spreads and finally forms a thin layer on the fiber surface. Since PSCC copolymer has a multitude of positively charged sites available for electronic neutralization, the particle can be strongly attached to the fibers even though an individual electronic attraction is weak. This feature also accelerates the polymer spreading under the influence of heat. Furthermore, the presence of multiple charge sites may prevent sizing reversion. Sizing reversion is thought to be due to the overturn of the polar groups to water molecules. In the case of PSCC sizing, even if there are some charged groups overturned, the rest are still able to work on anchoring the sizes to fiber surfaces and sizing will not be lost. This expectation was confirmed by the fact that there was no reduction observed on the HST value when the test was repeated ten days later.

### **Effect of Curing Time**

**Figure 5** shows the effect of curing time on PSCC sizing. The handsheets were sized with 0.5% PSCC and cured at 105<sup>0</sup>C. It can be seen that the sizing is more

developed as curing time increases. This can be explained by the dynamic effect on polymer mobility. One of the characteristics of polymer is the glass transition temperature ( $T_g$ ) at which polymer molecules are capable of moving. Because the glass transition temperature of polystyrene is about 105°C, the sizing cannot be developed until the polymer spreading occurs at high temperature. This is confirmed by the fact that without curing (i.e., curing time is zero), no paper sizing was observed through the sizing test. As curing time increases, the polymer molecules could have more chance to diffuse and spread under heat. As a result, the sizing is more developed.

### **Effect of pH**

The effect of pH on PSCC sizing was observed in the present study. The handsheets were sized under pH 6 and 7.5, respectively, with 0.5% PSCC and cured at 105°C for 30 min. As shown in **Figure 6**, HST values were the lower at lower pH condition. Indeed, this phenomenon was not expected to happen on PSCC. Since the quaternary ammonium has already been electronically saturated, changing pH condition should not affect its ionization or the degree of dissolution. Thus, the charge density and hydrophobicity of the polymer should not be affected either. The explanation of pH effect may be attributed to the changes of fiber surface chemistry. It is known that the surface charge on paper fibers is due to the ionization of surface functional group, such as carboxyl group (COOH). The pH has a profound effect on the state of these groups. Scott [2] pointed out that most of the carboxyl groups take on a proton and the charge becomes essentially zero at pH below 2.75. Conversely, at pH higher than 7, many of the carboxyl

groups are ionized and the fiber becomes more negatively charged. These changes of the surface charge with pH would affect the adsorption of polymer molecules on fibers. A high pH condition leads to a more negatively charged surface, a better retention, and therefore a higher sizing effect. At lower pH value, the less charged fiber could not attach as many polymers as it can at high pH; thus, the sizing efficiency is reduced.

### **Polymer Retention**

In order to investigate the PSCC retention on the handsheet directly, a UV/VIS diffuse reflectance spectroscopy was applied. It has been found that the integrated area under the UV spectra is correlated to the retained amount of polystyrene-based copolymer within the handsheets. For quantitative measurement, first, a set of handsheets without the addition of PSCC was made and air-dried; second, a series of 5-mL PSCC dispersions with known concentration were prepared and poured into the crystal dishes which had the same size as the handsheet; then, the handsheet was placed into the crystal dish evenly and absorbed the PSCC dispersion completely. It can be assumed that all the known amount of PSCC had been absorbed into the handsheet. Finally, the rewetted handsheet was cured at 105°C for 30 min. For each polymer retention level, five handsheets were prepared. During UV/VIS diffuse reflectance measurement, five places on each handsheet were detected. The average would be used. **Figure 7** shows the UV spectra of handsheets with various PSCC retention levels. As shown in **Figure 8**, the retention of PSCC in the handsheet is well correlated with the total UV absorption, that is, the integrated area under the UV spectrum. By using this correlation curve, the actual PSCC amount retained in the

handsheets can be obtained after measuring the sized handsheets by the UV/VIS diffuse reflectance method. **Figure 9** indicates the actual retained content of PSCC vs. its addition rate during papermaking. At a very low addition rate, little PSCC was retained. The results show zero percentage of polymer retained on handsheets. It may be partially due to the measurement limitation when a small amount of polymer presented in the handsheet. As the addition rate increases, the retained polymer amount increases; however, it shows the trend of leveling off as more polymers are added. It can be explained that when cationic PSCC particles are added to pulp, they anchor with negatively charged sites on fiber surfaces through electrostatic neutralization. As more positively charged particles occur in the pulp, the accessibility of anionic sites on the fiber surface are reduced, and then less amount of polymer can be retained.

In the meanwhile, the measurement of polymer retention supports the explanation of why PSCC has reduced sizing efficiency under lower pH condition. **Figure 10** demonstrates that with 0.5% addition rate, at pH 7.5, the actual retained content of PSCC was 0.38% based on the dry fiber weight, while at pH 6.0, only 0.34% polymer was retained. The reduced amount of polymer in handsheets is due to the surface chemistry change of the fiber. The lower the pH value, the less the ionization of carboxyl groups on fiber surface and therefore the negatively charged sites available for polymer attachment.

### **Polymer Coverage**

In order to further understand the PSCC sizing mechanism, efforts were made to investigate the effect of polymer coverage on the improvement of handsheet

hydrophobicity. For simplification, the anionic and smooth glass surface was applied as the model system. A predetermined amount of PSCC was dispersed within the defined surface area of the glass and heated overnight at 105<sup>0</sup>C. The amount of polymer per unit area was be calculated. The water contact angle was measured on the coated glass. As indicated in **Figure 11**, the contact angle of the glass increased significantly until the polymer coverage reached 8 mg/m<sup>2</sup> and then leveled off. This implies that the defined glass area had been fully covered by the polymer at this point. Theoretically, a maximum polymer adsorption occurs at 1 mg/m<sup>2</sup>. The fact that PSCC required a higher amount of polymer for complete coverage indicates that PSCC molecules are not fully spread during the practical sizing development. According to literature [14], the specific surface area of fiber is 1 m<sup>2</sup>/g and 8 m<sup>2</sup>/g for fine. Assuming 25% fine presented in the pulp that was used for handsheet making, a 1.2-g handsheet would have a surface area of 3.3 m<sup>2</sup>. For a full coverage on the handsheet, 0.22% PSCC (based on dry fiber weight) should be retained. This result is consistent with the fact that the paper sizing developed dramatically with 0.3% PSCC addition rate, that is, at 0.27% actual retention rate.

### **SEM Observation**

In the microscopic study on the PSCC sizing mechanism, the SEM technology was used to observe the PSCC particles and their rheological behavior under the influence of heat. **Figures 12** and **13** show the morphology of PSCC particles before and after heating. The melting and spreading of polymer particles formed an enlarged polymer film covering the Au-coated conductive surface, making the covered area darker due to polymer's

nonconductivity. It can be seen that the large particles did not spread completely; however, many much smaller dark spots presented in the after-heating photograph rather than in that of before heating. This may be due to the resolution limitation. It can be assumed that those small particles are dominant contributors to the sizing development.

## CONCLUSION

In summary, the polystyrene-based cationic copolymer (PSCC) could be used as an internal sizing agent. Paper sizing with PSCC was significant and it was a function of addition rate, curing temperature, and pH conditions. Polymer retention in the handsheet was obtainable by the UV/VIS diffuse reflectance method. The actual retained amount of polymer was the direct factor in determining its sizing efficiency. The hydrophobicity of handsheets could not be improved dramatically until the full coverage of polymer on fiber surface was reached.

Heat treatment was essential for PSCC sizing. The role of heating was to increase the spreading of size over fiber surfaces. The evidence from SEM observation supported this hypothesis.

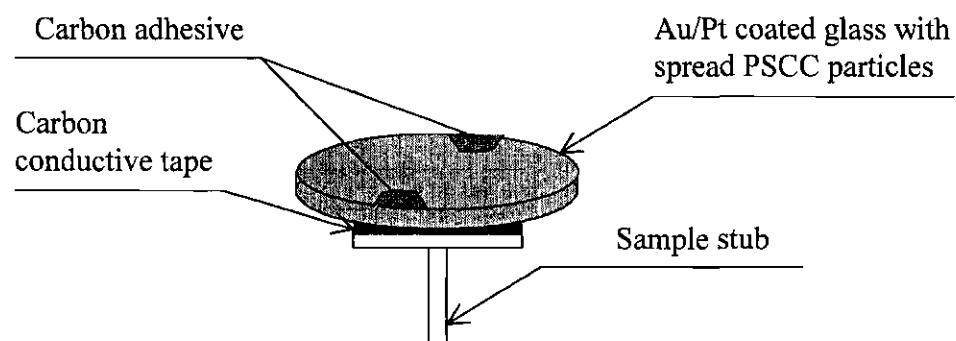
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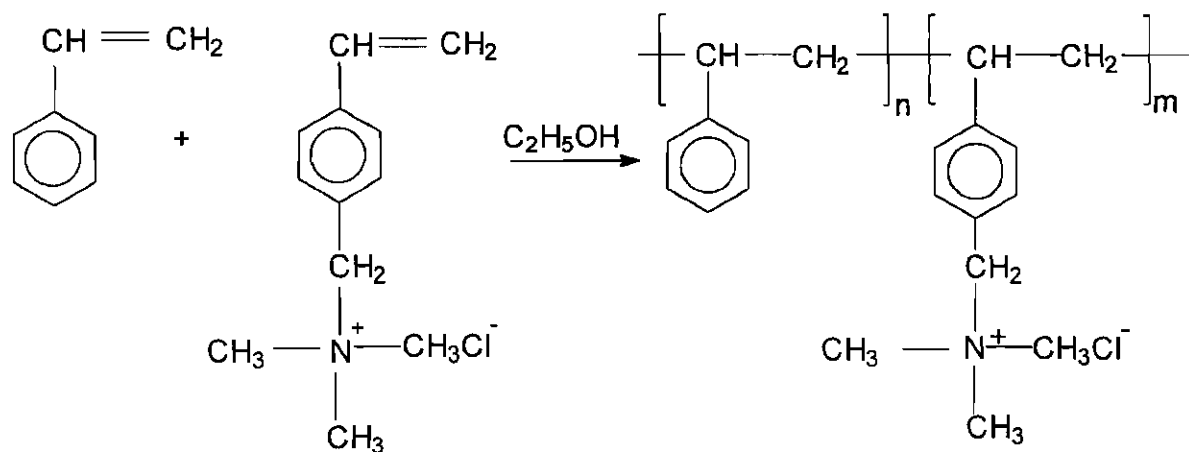


Composition		Amount
Monomer:	Styrene (mmol)	108
Comonomer:	VBTMAC (mmol)	12
Initiator	(mmol)	0.7
Solvent:	Ethanol (mL)	100
VBTMAC Ratio	(% total moles)	10
Temperature	(°C)	65
Reaction Time	(hr)	6

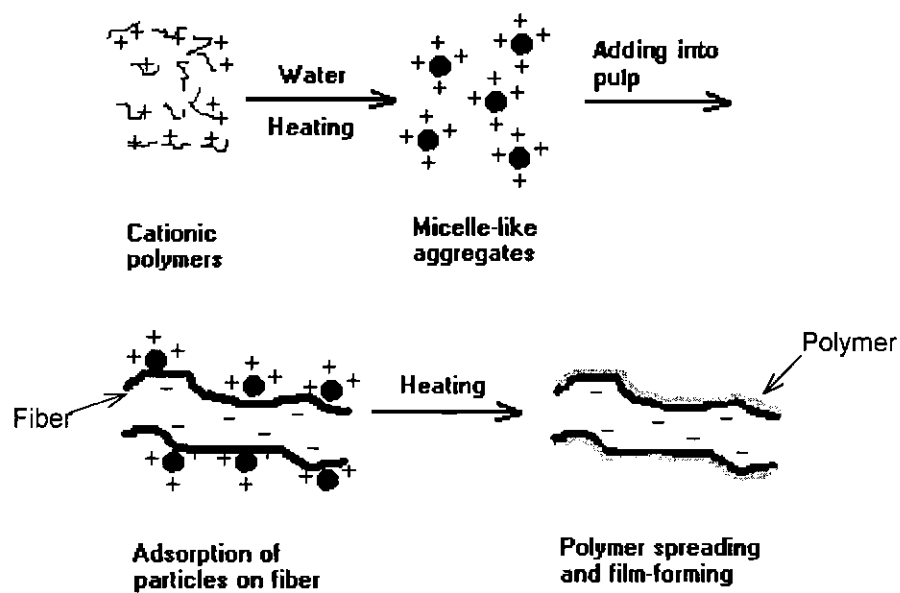
**Table 1. Synthesis Conditions**



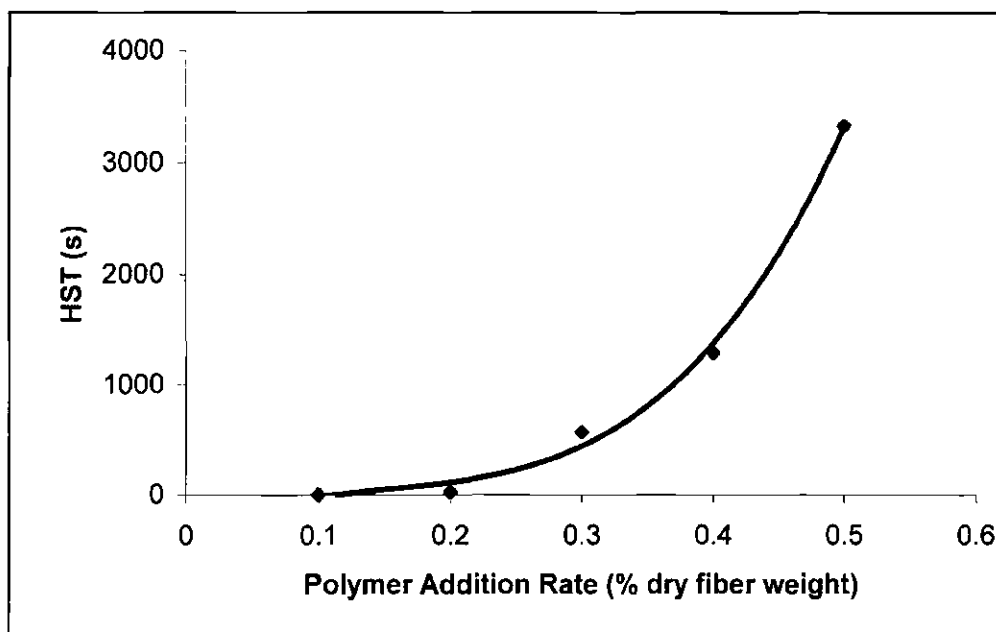
**Figure 1. SEM Sample Preparation**



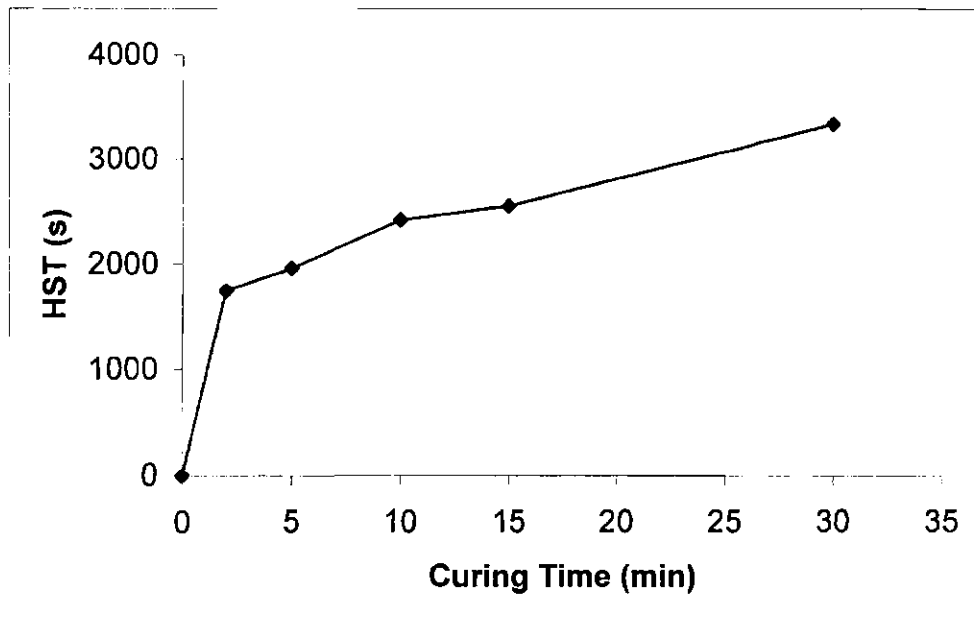
**Figure 2. Polymer Synthesis and Chemical Structure of PSSC**



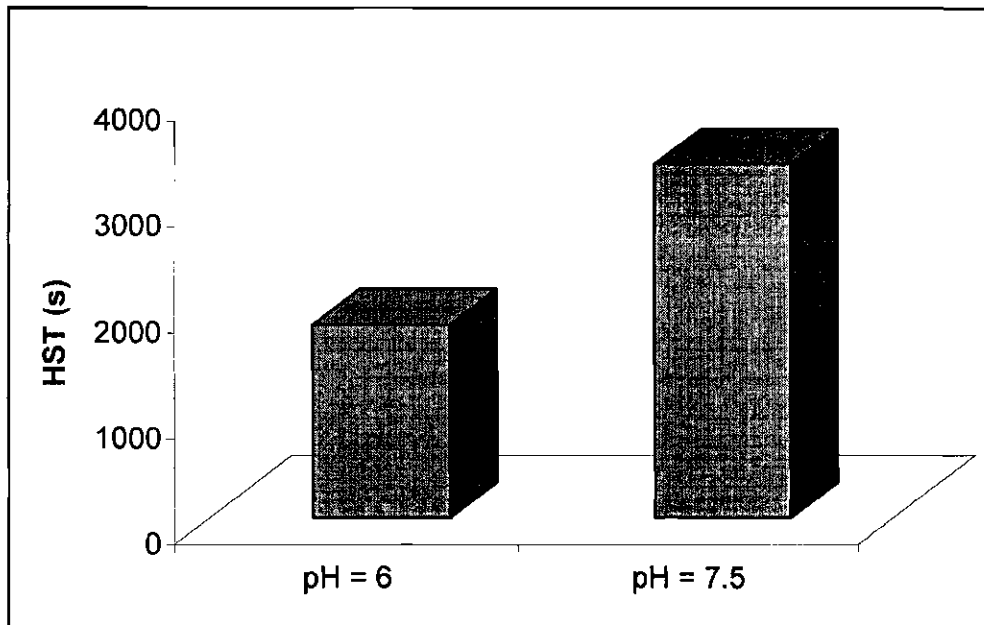
**Figure 3. Mechanism of Cationic Aggregates Formation  
and Application as Paper Sizing Agent**



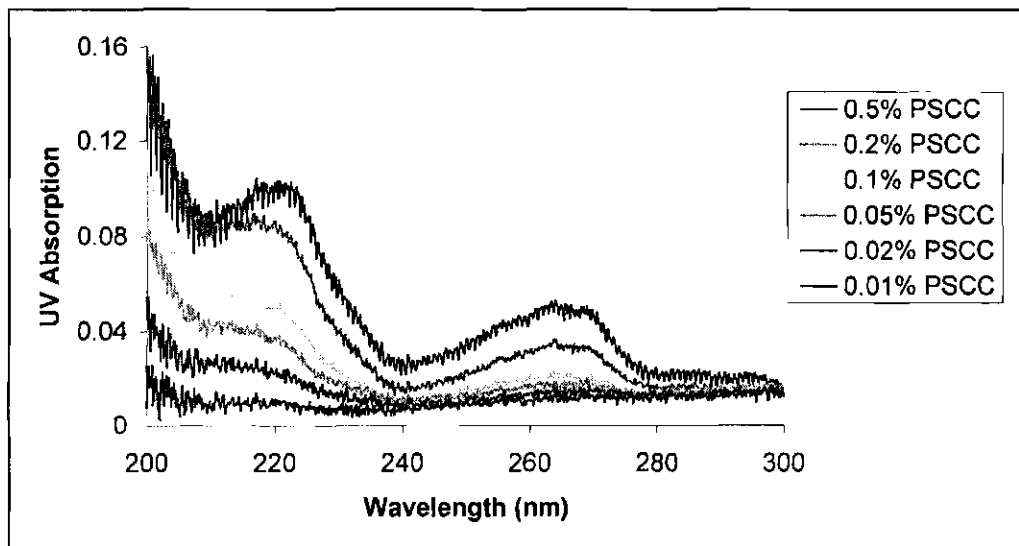
**Figure 4. Paper Sizing with PSCC**



**Figure 5. Effect of Curing Time on PSCC Sizing**

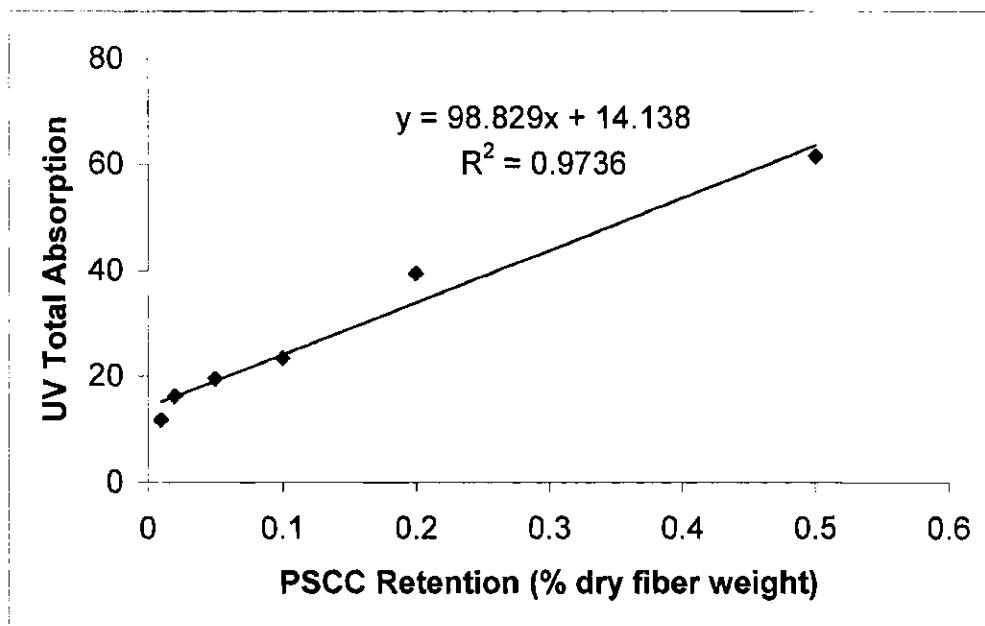


**Figure 6. Effect of pH Conditions on PSCC Sizing**

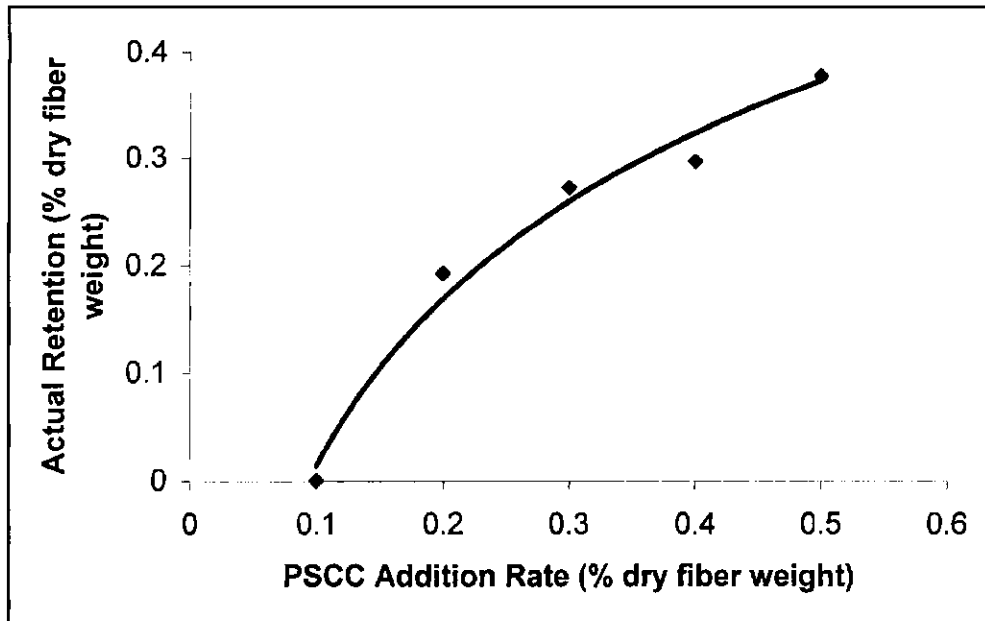


**Figure 7. UV Spectra of Handsheets with PSSC Retention**

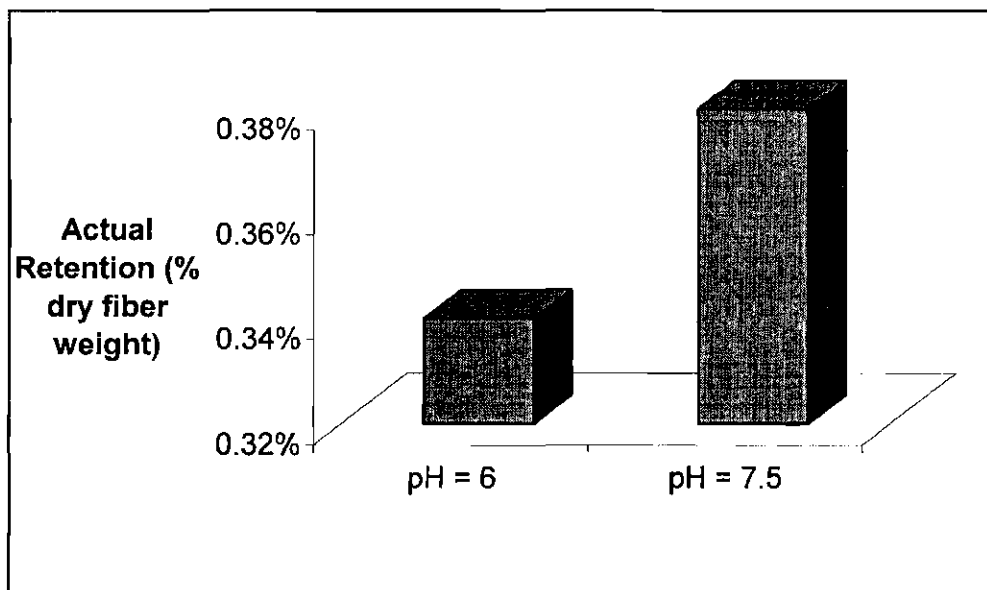




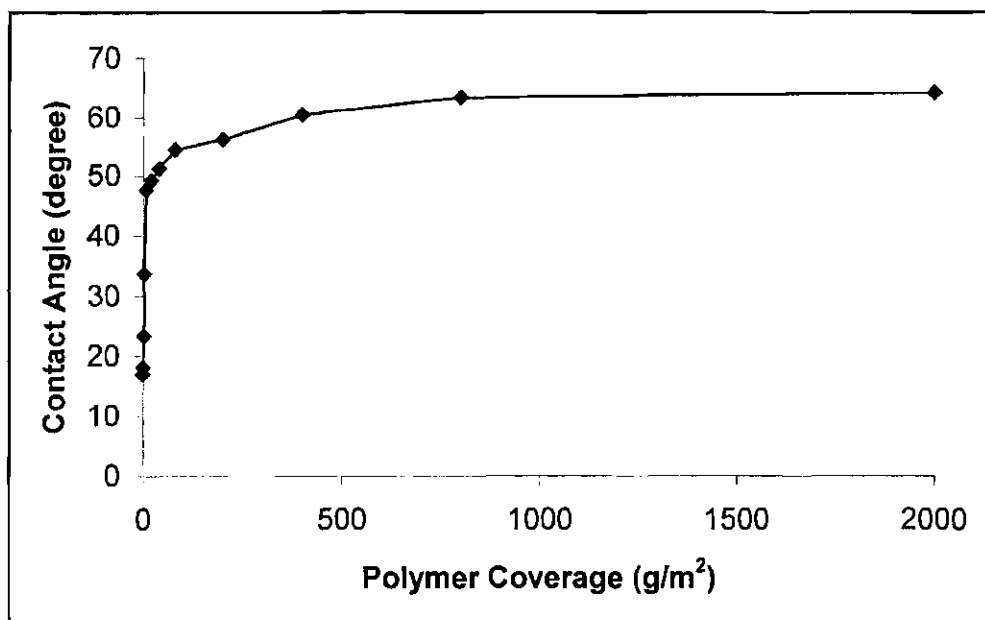
**Figure 8. Correlation between PSSC Retention and UV Total Absorption of Handsheet**



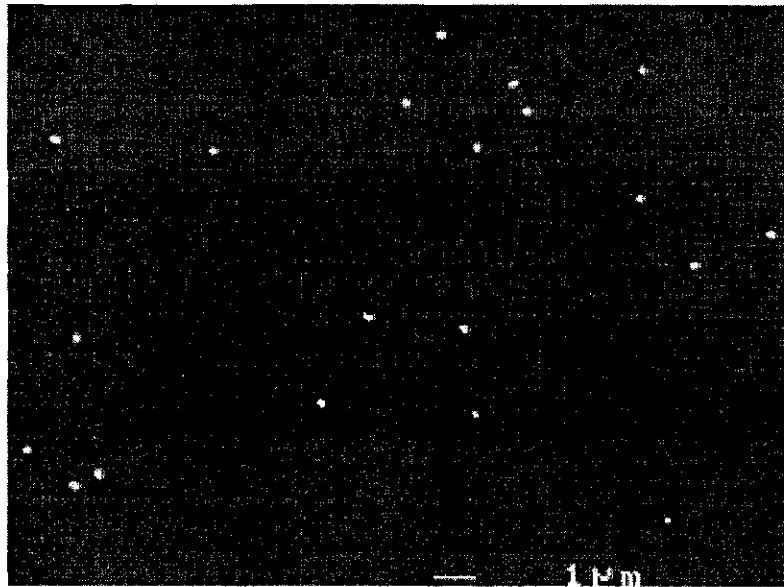
**Figure 9. PSSC Actual Retention vs. Addition Rate**



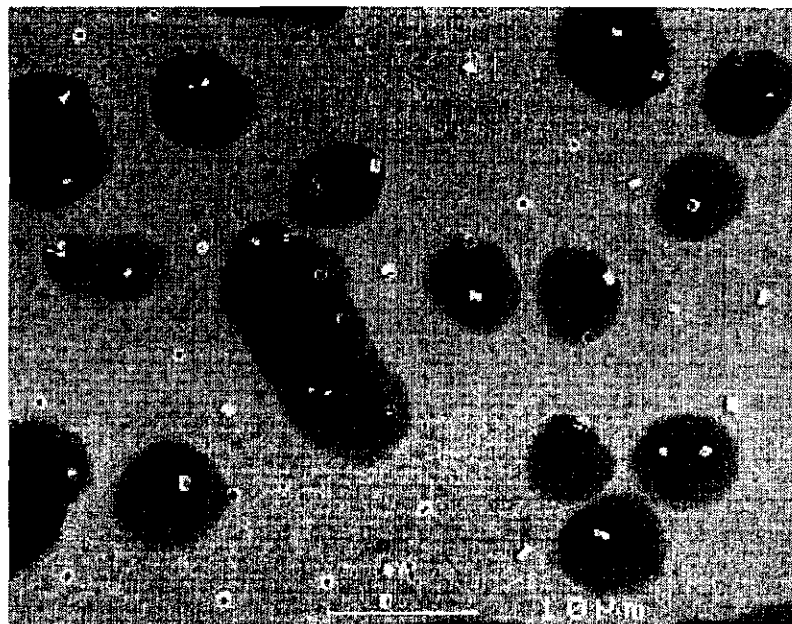
**Figure 10. Effect of pH on Polymer Retention**



**Figure 11. Polymer Coverage on Glass Surface**



**Figure 12. PSSC Particles Before Heating**



**Figure 13. PSSC Particles after Heating**